Solvent extraction of nickel(II) from sulphate solution using capric acid

A.SLIMANI and D.BARKAT*

Faculté des sciences et sciences de L'ingénieurs, Département de Chimie Industrielle,
Université de Biskra, Biskra, Algérie

Abstract

In this work we have studied the extraction of nickel(II) from a sulphate medium with capric acid noted (HA) in chloroform at 25°C in this study we will try to understand the behavior of this metal by varying a set of parameters like pH , the extractant concentration, polarity of solvent, effect of temperature on the extraction of this metal was also discussed. stoïchiometry of extracted species in the organic phase is $NiR_2(HR)_2$, the equilibrium constants have been evaluated as well as thermodynamic parameters $\Delta H°$, $\Delta S°$, and $\Delta G°$.

Keywords: capric acid; Nickell(II); sulphate medium; solvent polarity, temperature effect

1. Introduction

Pollution, nowadays, is an ever growing problem. It is due to the increase in energy and raw materials consumption, especially minerals which have become a real threat to our health. Therefore, it is high time we thought of disposing of their residues now dumped into the oceans, seas and rivers.

We didn't opt for solvent extraction arbitrarily. This method is inexhaustible and highly-performant with an outstanding track record as to the elimination of heavy metals such as nickel, cobalt, chromium.

carboxylic acids are organic compounds contain in their molecule the characteristic group (COOH) called carboxyle.They are characterized by their ability to form salts with number of metals, including alkali and alkaline earth [1-2]. Carboxylic acids have been studied as extractants for numerous metals and have shown to exhibit good extraction and separation efficiency [3].

Tanaka had studied extraction of copper(II), with capric acid dissolved in benzene, species formed in organic phase are $(CuA_2HA)_2$ [4], $(CoR_2)(HR)_4$for cobalt at lower loadings of the organic phase an a dimer $(CoR_2)_2(HR)_4$ at high loadings[5]. With capric acid nickel species formed in the organic phase are of the type $(NiR_22HR)_{2[}$6.]

Gindin et al have extensively studied the extractability of many many metals including zinc and cadmium with C_{7-9} alipahatic monocarboxylic acids; though have not always elucidated composition of extracted species [7].

2. Experimental

2.1. Reagents and solutions

Capric acid(98%, Fluka) used without further purification, organic diluents dichloromethane, toluene ,MIBKand cyclohexane were pre-equilibrated with aqueous solution which did not contain any metal. Sodium Hydroxide prepared in (0.1M) for the pH adjustment, nickel sulphate solution were prepared by dissolution of the respective sulphates in demineralized water(reagent grade extra pure from (Merck).

2.2. Extraction and analytical procedure

A mixture of equal volumes of nickel sulphate (6.810^{-3} M,400ppm) and capric acid(0.02M, 0.04M, 0.08M) dissolved in chloform,30ml of each one, is mechanically shaken up for 30 minutes in a thermostated vessel. The PH is adjusted by adding an NaOH solution (0. 1M).The ionic strength of the aqueous phase was assumed to be unity $[Na_2SO_4]=0.33M$. Decantation takes place within 15 minutes. The nickel concentration in the aqueous solution is photometrically calculated at 720nm using a Philips UV-VIS SP6-36.The organic phase concentration is the difference between the initial concentration of nickel in the aqueous solution, and after the extraction.

3. Discussion of results

3.1. General treatment of the extraction equilibrium of nickel(II) with capric acid

In the most generalized way the overall extraction of a metal ion from an aqueous layer with an acidic extractant may be written as follows:

$$\mathrm{M_{aq}} + \frac{\mathrm{n+m}}{2}\,\mathrm{(HA)_{2,\,org}} \rightleftarrows \frac{1}{\mathrm{j}}\,\mathrm{(MA_n.\,mHA)_{j+}nH^+_{aq}} \ (1)$$

The complex $\mathrm{(MA_n.\,mHA)_j}$ will further be denoted as c. we define an overall equilibrium constant for this reaction:

Equilibrium constant in terms of activity:

$$\mathrm{K}' = \frac{[\mathrm{C}]_{\mathrm{org}}^{\frac{1}{\mathrm{j}}}\,[\mathrm{H}]_{\mathrm{aq}}^{\mathrm{n}}}{[\mathrm{M}]_{\mathrm{aq}}\,[(\mathrm{HA})2]_{\mathrm{org}}^{\frac{(\mathrm{n+m})}{2}}} \cdot \frac{\gamma \mathrm{C},_{\mathrm{org}}^{\frac{1}{\mathrm{j}}}\,\gamma^{\mathrm{n}}\,\mathrm{H},_{\mathrm{aq}}}{\gamma_{\mathrm{M,aq}}\,\gamma(\mathrm{HA})_{2,\mathrm{org}}^{\left(\frac{\mathrm{n+m}}{2}\right)}} = \mathrm{KB}(2)$$

The results of the measurements generally are values of the analytical distribution coefficient, defined as:

$$\mathrm{D} = \frac{[\mathrm{M}]_{\mathrm{org}}}{[\mathrm{M}]_{\mathrm{aq}}} \qquad (3)$$

$$[\mathrm{C}]_{\mathrm{org}}^{\frac{1}{\mathrm{j}}} = \left[\frac{1}{\mathrm{j}}\mathrm{M}\right]^{\frac{1}{\mathrm{j}}} = [\mathrm{M}]_{\mathrm{org}}^{\frac{1}{\mathrm{j}}}\left(\frac{1}{\mathrm{j}}\right)^{\frac{1}{\mathrm{j}}} = [\mathrm{M}]_{\mathrm{org}}\,[\mathrm{M}]_{\mathrm{org}}^{\frac{(1-\mathrm{j})}{\mathrm{j}}}\left(\frac{1}{\mathrm{j}}\right)^{\frac{1}{\mathrm{j}}}$$

Further, it follows from eq.3that $[\mathrm{M}]_{\mathrm{org}} = \mathrm{D}[\mathrm{M}]_{\mathrm{aq}}$, and hence

$$[\mathrm{C}]_{\mathrm{org}}^{\frac{1}{\mathrm{j}}} = \mathrm{D}[\mathrm{M}]_{\mathrm{aq}}\,[\mathrm{M}]_{\mathrm{org}}^{\frac{(1-\mathrm{j})}{\mathrm{j}}}\left(\frac{1}{\mathrm{j}}\right)^{\frac{1}{\mathrm{j}}} \qquad (4).$$

Substitution of eq.4 into 2 gives for K’

$$\mathbf{K}' = \frac{\left\{\mathrm{D}[\mathrm{M}]_{\mathrm{org}}^{\frac{(1-\mathrm{j})}{\mathrm{j}}}\left(\frac{1}{\mathrm{j}}\right)^{\frac{1}{\mathrm{j}}}\right\}[\mathrm{H}]_{\mathrm{aq}}^{\mathrm{n}}}{[(\mathbf{HA})_{\mathbf{2}}]^{\frac{(\mathbf{n}+\mathbf{m})}{\mathbf{2}}}}\,\mathbf{B}$$

Or, taking logarithms :

$$\log\mathrm{D} = \log\mathrm{K}' - \log\mathrm{B} + \left(\frac{\mathrm{j}-1}{\mathrm{j}}\right)\log[\mathrm{M}]_{\mathrm{org}} + \left(\frac{1}{\mathrm{j}}\right)\log\mathrm{j} + \mathrm{npH} + \left(\frac{\mathrm{n}+\mathrm{m}}{2}\right)\log(\mathrm{HA})_2 \quad .(5)$$

Nomenclature:

M : metal ion.

HA : acidic extractant.

A : anion of extractant.

B : activity coefficient of product.

[HA] : initial extractant concentration.

$\gamma_{\mathrm{a.b}}$: activity coefficient for the species a in phase b.

n : number of extractant groups bound to M in a « salt like » manner.

m : number of extractant molecules bound as solvation molecules.

j : degree of polymerization of the extracted complex.

C : extracted complex.

K : equilibrium constant with respect toconcentrations.

K’ : equilibrium constant with respect to activities.

3.2. Extraction concentration and pH dependence

One of the main objectives of this study is to determine the stoïchiometry of the extracted species for this purpose experimental results are arranged according to equation 5.

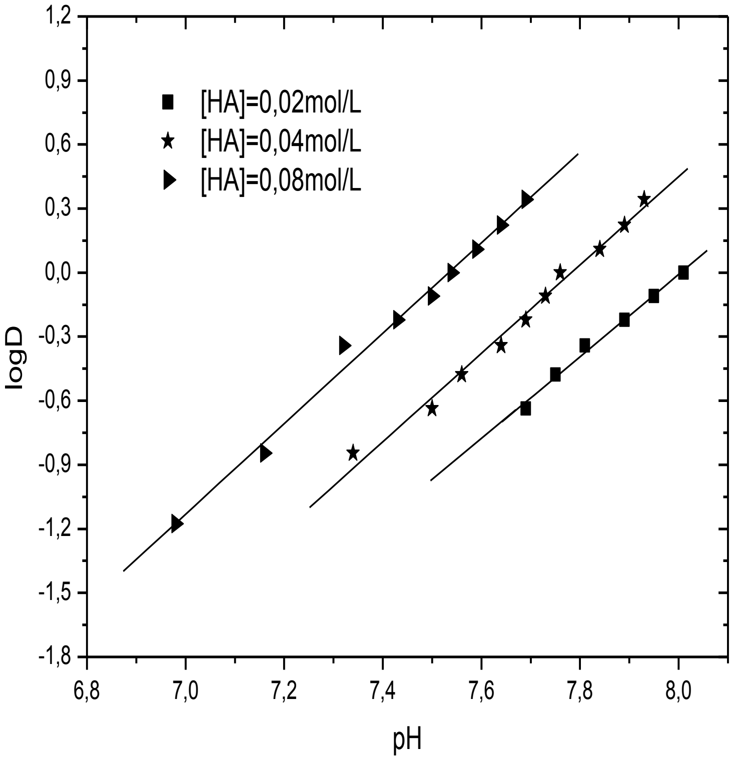

Figure 1. Effect of pH on the extraction of nickel(II) from sulphate medium with capric acid dissolved in chloroform.

Figure 1, show the relationship between logD and pH to extract nickel(II) at three different concentrations of capric acid (0.01,0.02,0.08) as straight lines with a slope of 2 for each one of the lines. Taking equation (5) as reference and by application of the slope analysis technique, n=2 we have found that the two de-protonated capric acids have bonded with the nickel cation during the extraction process, the logarithmic equilibrium constant of nickel(II) with capric acid in chloroform was calculated ($\log K_{ex}$=-12.5).

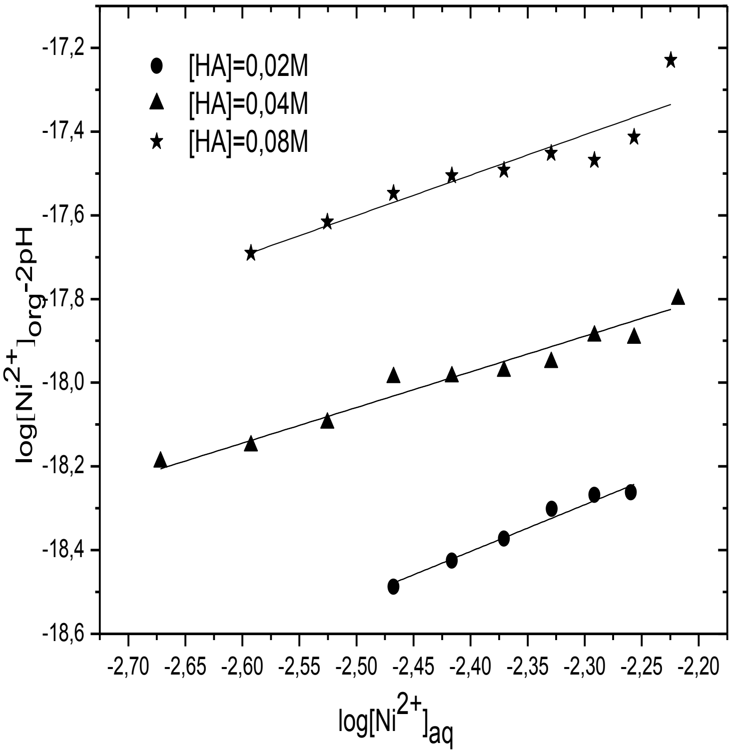

Figure 2. Degree of polymerization of nickel extracted complex in chloroform $[NiSO_4]$=0.33M

The extracted species in the organic phase are 1/j(NiA_2mHA); $_j$ j being the degree of polymerization of the Nickel-Capric acid compound; were calculated from the log($[N\,i]_{org}[H^+]^2$) graph versus log($[N\,i]_{aq}$ as shown in figure 2, We got a straight lines with a slope of the unity for each one this means j=1.Therefore, the extracted species are monomers of the (NiA_2mHA) type. we have to say that extraction with fatty acids like capric acid proceeds by cation exchangers where proton of the acid is exchanged by metal ion[8].

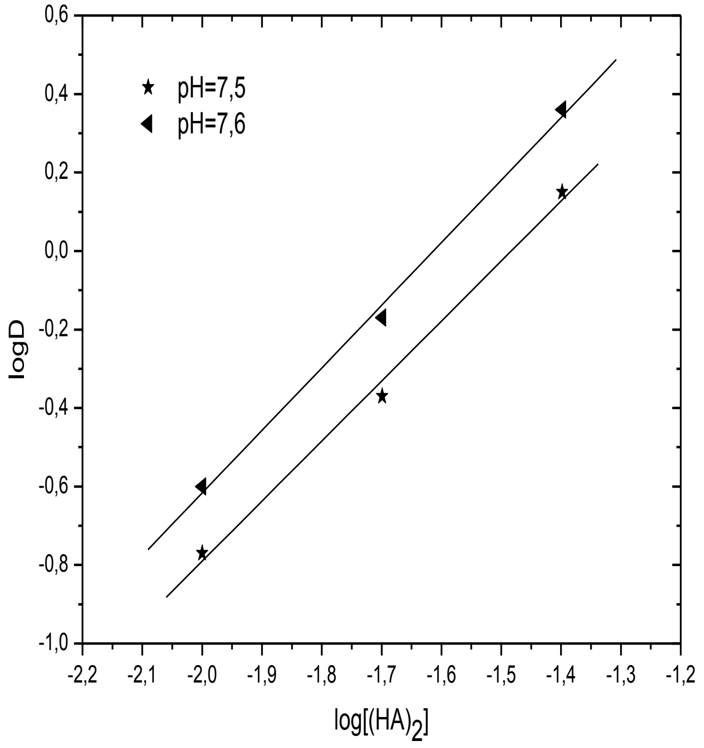

Figure 3. Effect of the extractant concentration on the extraction of Nickel(II) in chloroform at 25°C

The m number of capric acid involved in the monomeric species was determined from the logD slope versus log[$(HL)_2$] (equation5) . $(HL)_2$ in the organic phase is assumed to be ($0.5C_{HL}$) given that C_{HL} is the total acid concentration.from figure3 the calculated slope value is 2 this lead to (n+m)/2 equal to 2 we conclud that m takes 2 as a value .Three unknown are determined (n=2,j=1,m=2) which allow us to know the extracted complex stoïchiometry which is $NiA_2(HA)_2$ this stoïchiometry was observed in the extraction of nickel with cyanex272[9]. Necla GÜNDÜZ and Nihal SÖKMEN have studied the extraction of nickel with octanoic acid, decanoic acid and lauric acid in kerosene they found $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$ possible structures in octanoic acid(0.5M-1M) they also found $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$ as possible structures of extracted nickel in decanoic acid(0.5M-1M) in lauric acid they found the following stoïchiometries NiA_2, NiA_2HA [10].

The electronic absorption spectrum of the extracted complex in the organic phase (figure4) is characterized by the presence of a well-defined band and a shoulder in the visible region corresponding to the following wavelengths: λ1 396nm and λ2 671nm which ensure octahedrical geometry of the extracted complex and a chromophore (NiO_4)[3].

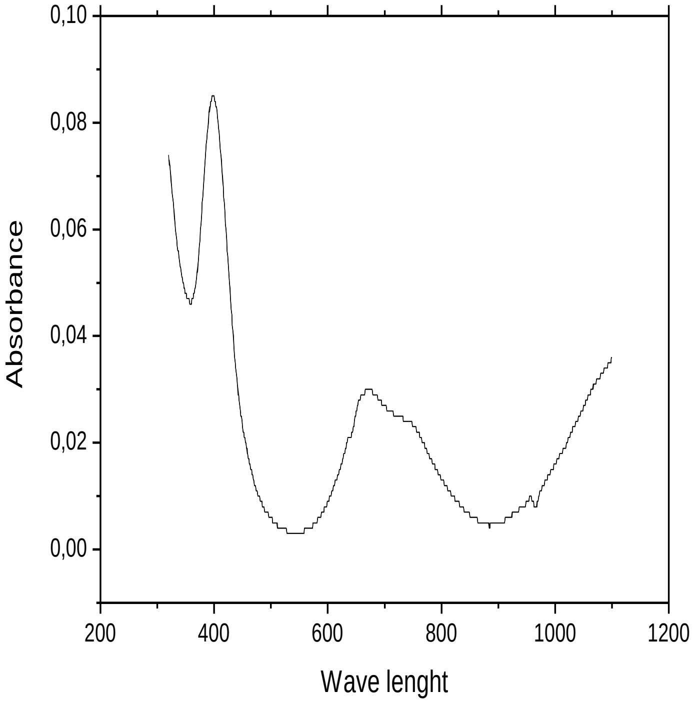

Figure 4. The electronic absorption spectrum of the extracted complex of nickel(II) in the organic phase.

3.3. Effect of diluents

It is well known that diluents plays an important role in solvent extraction by affecting the efficiency of the extraction process [8] extraction of nickel(II) with capric acid was elaborated by using chloroform, cyclohexane, toluene and MIBK. AdjelStudied the effect of diluents on the extraction of copper ,cobalt and nickel[3]. Ghebghoub and Barkat studied the effect of diluents upon the extraction of copper(II) with di(2-ethylhexyl)phosphoric acid[11].

The best extraction order was: cyclohexane>toluene> chloroform>MIBK.

.

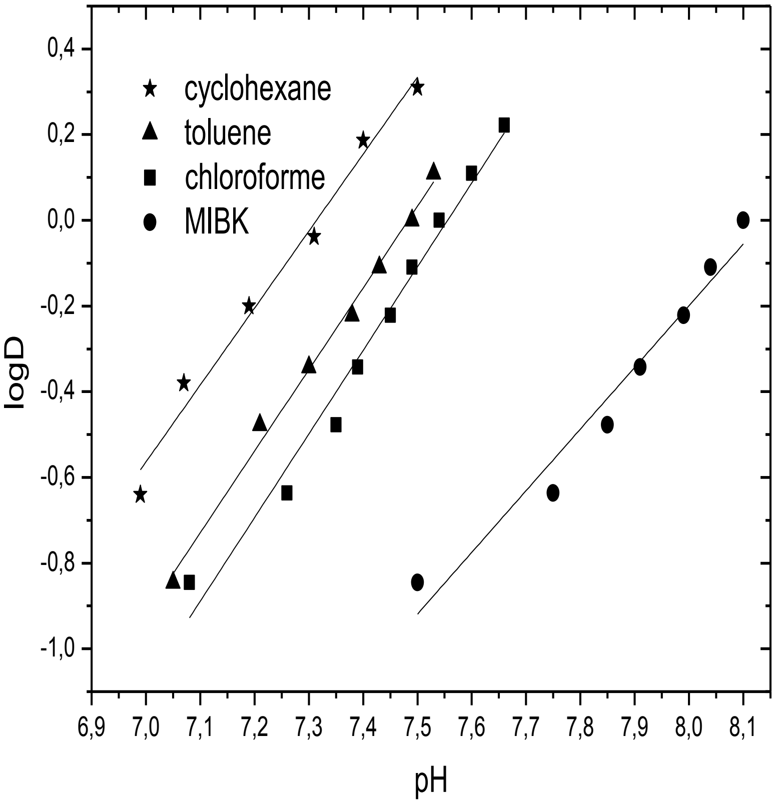

Figure 7. Extraction of nickel(II) with capric acid dissolved in chloroform in different solvents

3.4. Effect of temperature

Relationship between logD and pH during the extraction of metal at different temperatures is represented in figure 6. From the figure it is clear that increase in temperature leads to an increased extraction. The values of Kex at different temperatures calculated from the following equation

$$\text{Log } K_{ex}=\log D_{Ni}-2\log [HL]_{org}-2pH \qquad (6)$$

The relation between $\log K_{ex}$ and thermodynamic parameters can be expressed as

$$\log K_{ex} = \frac{-\Delta H°}{2.303RT} + \frac{-\Delta S°}{2.303R} \qquad (7)$$

Table 1. Values of the extraction constants of nickel(II) at different temperatures.

T(K)	**283**	**293**	**303**	**313**	**323**
$\log K_{ex}$	**-12.9**	**-12.7**	**-12.1**	**-11.9**	**-11.74**

ΔH°: is extraction enthalpy of nickel(II).

ΔS°: is extraction entropy of nickel(II).

ΔG°: is extraction free energy of nickel(II).

T(K): is chosen temperature .

R : is gas constant ($8.31 JK^{-1}mol^{-1}$).

When plotting $\log K_{ex}$ versus 1/T we ger a slope of $\frac{-\Delta H°}{2.303R}$ and a y-intercept of $\frac{-\Delta S°}{2.303R}$

The values of ΔH°, ΔS°and ΔG° are easily calculated and listed in table2

Table 2. Thermodynamic parameters for nickel(II) extraction

ΔH°(kJ/mol)	ΔS°(JK^{-1}/mol)	ΔG°(JK^{-1}/mol)
56.15	**-48.80**	**71.13**

From thermodynamic results we conclude that extraction of nickel(II) with capric acid dissolved in chloroform is is endothermic (ΔH°=56.15 >0), (ΔG°=71.13>0) the reaction is not spontaneous.

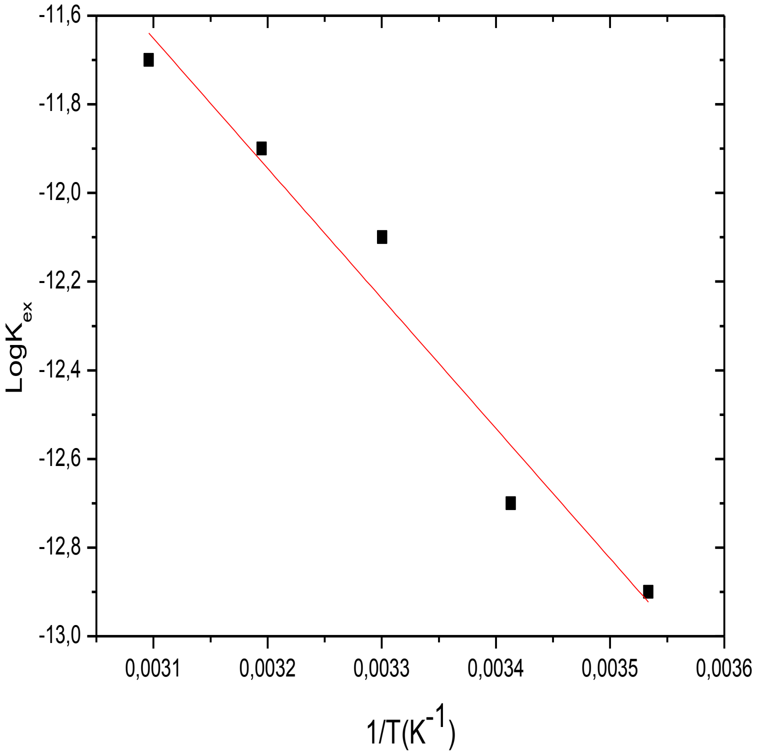

Figure 8. Variation of equilibrium constant of nickel extraction with temperature

4. Conclusion

In this research we have used capric acid to extract nickel(II) from a sulpahate medium, and we found that this process depends on pH, extractant concentration. Extracted species have an $NiR_2(HR)_2$ stoïchiometry [9].

Extraction of nickel vary between highly-polarized solvents, average and the low polarized solvents (it don't follows polarity order) .

Increasing of temperature had a positive effect in the elimination of the metal [8].

The elimination rate reached 80% by simple extraction; it even attained 95% just by varying the temperature. From thermodynamic parameters we concluded that reaction is endothermic.

In the end, we can state that the goal of this study is to observe the nickel behavior extracted in the capric acid and according to different variables the effect of which on extraction were already studied. The aim is to survey this metal and come up with a scholarly work to further examine its unexplored aspects.

References:

[1] D. Barkat, M. Kameche, *phy. Chem. Liq*.,**45**,289 (2007).

[2] Dyrsen,D., *Acta chem. Scand*., **11**,1771 (1957).

[3] F. Adjel, D. Barkat. *J. Coord. Chem*.,*64*, 574 (2011).

[4] M. Tanaka, T. Niinomi. *J. Inorg. Nucl. Chem*., **27**, 435 (1965).

[5] Sh G. Beheir, M. Aziz, K. Shakir. *J. Radio. Nuclear. Chem*., **174**, 13 (1993).

[6] M. Tanaka, N. Nakasuka, S. Sasane. *J. Inorg. Nucl. Chem*., **31**, 2594 (1969).

[7] N. NAKASUKA , Y. Mitsuoka, M. Tanaka. *J. Inorg. Nucl. Chem*., **36**., 431 (1974).

[8] A. Aidi, D. Barkat. *J. Coord. Chem*.,**63**,4136(2010).

[9] K. Sarangi, B.R. Reddy, R.P. Das. *Hydrometallurgy*, **52**, 253 (1999).

[10] N. GÜNDÜZ , N. SÖKMEN. *Commun. Fac. Sci. Univ. Ank. Series B*., **33**.,15 (1987)

[11] F. Ghebghoub, D. Barkat. *J. Coord. Chem*.,**62**, 1449 (2009).

---

i

[ii]